

# Stationary Metastability in an Exact Non-Mean Field Calculation for a Model without Long-Range Interactions

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## Abstract

We introduce the concept of stationary metastable states (SMS's) in the presence of another more stable state. The stationary nature allows us to study SMS's by using a restricted partition function formalism as advocated by Penrose and Lebowitz and requires continuing the free energy. The formalism ensures that SMS free energy satisfies the requirement of thermodynamic stability everywhere including  $T = 0$ , but need not represent a physically observable metastable state over the range where the entropy under continuation becomes negative. We consider a 1-dimensional  $m$ -component axis-spin model involving only nearest-neighbor interactions, which is solved exactly. The high-temperature expansion of the model represents a polymer problem in which  $m$  acts as the activity of a loop formation. We follow deGennes and treat  $m$  as a real variable. A thermodynamic phase transition occurs in the model for  $m < 1$ . The analytic continuation of the high-temperature disordered phase free energy below the transition represents the free energy of the metastable state. The calculation shows that the notion of SMS is not necessarily a consequence of only mean-field analysis or requires long-range interactions.

## I. INTRODUCTION

Supercooled and superheated states are ubiquitous in Nature, even though they *cannot* be rigorously derived from *equilibrium* statistical mechanics [1]. Their observation is usually justified by appeal to the “van der Waals loop” in the celebrated van der Waals equation for the liquid-gas transition. The existence of the loop violates the fundamental property that the partition function (PF) be maximized or the free energy be *convex*. Despite this, metastable states appear not only in many other mean-field theories such as the Bragg-Williams theory [2], but can easily be prepared in the laboratory. There are usually two different mechanism operative in metastable states. There is usually a “fast” mechanism (time scale  $\tau_f$ ) to create a metastable state in the system, followed by a “slow” mechanism (time scale  $\tau_s$ ) for nucleation of the stable phase and the eventual decay of the metastable state. For the metastable state to exist for a while, we need to require  $\tau_s > \tau_f$ . In approximate theories, the thermodynamic functions for the metastable states are taken as the extrapolation of the functions from the nearby equilibrium states. However, metastable states in real systems always have time-dependence associated with them. Thus, the metastable state represented by extrapolation can only represent the *stationary* limit ( $\tau_s \rightarrow \infty$ ) of experimentally observed metastable states; see also [3]. However, it has been suggested that the extrapolation is possible only because of the mean-field approximation, and would not be possible in real systems due to a singularity in the thermodynamic functions [4]. The presence of the stable phase above some critical size in the metastable state is responsible for the decay of metastable states and for the *essential singularity* in the free energy [4]. The singularity is absent in mean-field theories or theories with long-range interactions. Accordingly, the existence of SMS (no time-dependence) is commonly considered a mean-field consequence or due to long-range interactions so that one should not see-

SMS's in real systems [1]. On the other hand, what one observes in experiments are (time-dependent) metastable states. Since essential singularities are almost impossible to detect experimentally, it is not surprising that the extrapolation is possible, at least from the experimentalist's point of view.

In many cases, metastable states like supercooled liquids and glasses can remain stable for a long period of times [5, 6]. This should be contrasted with metastability at high temperatures in the liquid-gas transition that do not share this property. Thus, for supercooled liquids,  $\tau_s \gg \tau_f$ . This can be understood by the high viscosity observed in supercooled liquids, which slows down the growth of the stable phase nuclei. There is another remarkable difference. Supercooled liquids such as viscous liquids usually do not (but very well could, as was seen recently [7]) exhibit spinodals, while supercooled vapor and superheated liquid invariably do. Rather, viscous liquids undergo a glass transition at low temperatures, about two-thirds of their melting temperature  $T_M$ , provided the liquid is cooled in a way that crystallization does *not* intervene. Here, the crystal phase (CR) represents the more stable phase, and care must be exercised to forbid its nuclei to form while cooling the viscous liquid. This makes the decay of the metastable state even less probable, and strengthens the inequality  $\tau_s \gg \tau_f$ . Thus, it is safe to treat viscous liquids as stationary metastable states (SMS's), which can then be described by equilibrium thermodynamics under the *restriction* that the crystal phase is not allowed. It is these SMS's that are of interest in this work. It is the hope that the study of SMS will throw some light on the properties of observed metastable states in the form of viscous fluids. In particular, the extrapolated free energy below the melting temperature can be used to describe supercooled liquids.

However, even if extrapolation is possible, one must still argue that the thermodynamic functions describe the stationary limit of experimentally observed metastable states. Under what condition(s) can one demonstrate this association to be valid?

FIG. 1: Schematic form of the generic entropy functions for various possible states.

While there is no rigorous theory of such SMS's at present, there are some valuable approaches available in the literature. One such approach to describe SMS is to use the PL formalism of Penrose and Lebowitz (PL) [1] using *restricted ensemble* method, which we modify and adapt for our case below. The modification is the following. The decay of the metastable states (to the stable state) in the PL formalism will be *completely* suppressed in order to make them stationary. Thus, nucleation of the stable phase will not be allowed in our study. This is consistent with Maxwell's idea [8] that to observe metastable states, we must ensure that the stable phase is not present. The properties of the SMS are what PL call the static or reversible properties [1].

An alternative scenario for extrapolation is by analytically continuing the eigenvalues of the transfer matrix as presented in [9], which attempts to accomplish the same as the restricted ensemble does but in a somewhat direct fashion.

#### A. Schematic Entropy Functions under Continuation

In the PL approach, only certain microstates out of all are allowed, the prescription of which is discussed in [1]. The restricted microstates are used to define a restricted partition function, which is then used to study metastable states. This is schematically shown in Fig. 1, where the curve OHAB represents the entropy function  $S_{\text{ord}}(E)$  for the ordered crystal state, while DH'AO'K represents the entropy  $S_{\text{dis}}(E)$  associated with the disordered liquid state. The entropy as a function of  $E$  must be thought of as the entropy in the microcanonical

ensemble [10], which must be at its maximum in the equilibrium state. Since a SMS is not an equilibrium state in the unrestricted ensemble, its entropy at some  $E$  *cannot* exceed the entropy of the corresponding equilibrium state at the same  $E$ . It is clear, therefore, that at lower energies, the ordered state must have higher entropy, while at higher energies the disordered state must have higher entropy. On the other hand, if a time-dependent metastable state is prepared under the constraint that the stable phase is not allowed, then the entropy function of such a metastable state will be represented schematically by FG. The three free energies corresponding to the above entropy functions are shown in the inset. A consequence of the entropy maximization principle noted above is that the free energy  $F_{\text{dis}}(T)$  of SMS *cannot* be lower than the free energy  $F_{\text{ord}}(T)$  of CR at the same temperature  $T$ . This explains the form of the free energy in the inset. The slope of the tangent line HH' gives the inverse melting temperature, while the slope of the tangent line OO' gives the inverse temperature at which the free energy DO'CK in the inset is equal to the free energy of the crystal phase at absolute zero ( $T = 0$ ). The slope of the entropy at K is shown to be finite, as opposed to the infinite slope at O. This point will be discussed further below.

The question that naturally arises is whether the above extrapolation is possible. It should also be noted that the extrapolation of the free energy does not guarantee that metastable states associated with this extension exist in the model. This will become clear in the following. Thus, the other important issue is to understand the condition under which the extrapolation will represent the stationary limit of the metastable states that might be observed. To answer these questions, we borrow ideas from both approaches mentioned above and develop an approach, which is then tested by considering a 1-dimensional lattice model. This model has only nearest-neighbor interactions, and is solved exactly by the use of the transfer matrix. We find that the extrapolation can be carried out without any ambiguity to describe stationary metastable states (SMS) in this case. Thus, stationary metastability can exist even in non-mean-field theories and without long-range interactions, which is our main result. We further show that the extrapolation yields a thermodynamically stable SMS free energy, at least mathematically (see below for details), all the way down to absolute zero. However, the continuation cannot represent any metastable state at very low temperatures when the entropy becomes negative, and must be stopped. At this point, the continuation must be replaced by what is conventionally called an ideal glass; see below. This situation should be contrasted with the termination of a metastable state in a spinodal. The point where the entropy vanishes is not a spinodal.

## B. Fundamental Postulate

We assume the *existence* of SMS's, so that the partition function (PF) formalism can be applied. The need for the assumption is easy to understand. At present, our understanding of whether equilibrium (lowest free energy) states can be demonstrated to exist mathematically even in simple models is too limited. We should recall that the existence of equilibrium states is taken for granted as a *postulate* in statistical mechanics and thermodynamics, where it is well known that it is extremely hard to prove their existence. We quote Huang [11]: "Statistical mechanics, however, does not describe how a system approaches equilibrium, nor does it determine whether a system can ever be found to be in equilibrium. It merely states what the equilibrium situation is for a given system." Ruelle [12] notes that equilibrium states are defined *operationally* by assuming that the state of an isolated system tends to an equilibrium state as time tends to  $+\infty$ . Whether a real system actually approaches this state cannot be answered.

The problem becomes more complicated for SMS's like supercooled liquids in which, at least at low temperatures, the relaxation becomes very sluggish and it is highly likely that the appropriate relaxation time  $\tau_f$  indeed tends to  $+\infty$ . In other words, such an SMS may not even be observed in a finite amount of time, even though associated time-dependent metastable states can certainly be observed. Even in this case, the study of the long-time limit of metastable states still has a predictive value, and can be carried out using the statistical mechanical formalism.

## C. Reality Condition

For the microstates to exist in Nature, it is evident that  $W(E)$ , the number of microstates of energy  $E$ , must satisfy the *reality condition*  $W(E) \geq 1$  [so that the entropy  $S(T) \geq 0$ ] even in the restricted ensemble. However, a state with *negative entropy* can emerge under extrapolations of the free energy. If it happens that the extrapolation results in a negative  $S(T)$  at low temperatures, this will indicate that the extrapolation no longer represents real microstates, and the system could not be found in those microstates in Nature.

There are two *independent* aspects of thermodynamics and statistical mechanics. The first one is the requirement of *stability* according to which thermodynamic quantities like the heat capacity, the compressibility, etc. must never be negative. The other aspect, independent of the stability criteria, is the *reality* condition that ensures that such states occur in Nature [13]. The mathematical extension of the free energy of the disordered phase, while always satisfying the stability criteria everywhere ( $T \geq 0$ ), need not satisfy the reality condition, as our example will show below.

## II. EQUILIBRIUM FORMULATION

### A. Canonical Partition Function

We consider a system composed of  $N$  particles confined in a given volume  $V$  and at a given temperature  $T$ . The canonical PF is given by

$$Z_N(T) \equiv \text{Tr } W_N(E) \exp(-\beta E), \quad (1)$$

where  $\text{Tr}$  is over all possible values of the energy,  $W_N(E)$  is the number of microstates of energy  $E$  [14], and  $\beta \equiv 1/T$ ,  $T$  being the system temperature in the units of the Boltzmann constant  $k_B$ . We do not explicitly show the volume-dependence. We also introduce the adimensional free energy (without the conventional minus sign)

$$\Omega_N(T) \equiv \ln Z_N. \quad (2)$$

For microstates to exist in Nature,  $W_N(E) \geq 1$ ; hence the corresponding entropy  $S_N(E) \equiv \ln W_N(E) \geq 0$ . Whether this remain true for the analytic continuation remains to be seen.

### B. Thermodynamic Limit

The thermodynamic limit is obtained by taking  $N \rightarrow \infty$ , and  $V \rightarrow \infty$ , keeping  $v \equiv V/N$  fixed. The limit is taken by considering the sequence formed by

$$\omega_N(T) \equiv (1/N)\Omega_N(T),$$

for different values of  $N$  as  $N \rightarrow \infty$ . The volume must be changed according to  $V = vN$ . For proper thermodynamics, the limit of the sequences must exist, which we assume and denote it by  $\omega(T)$ . The corresponding Helmholtz free energy is  $f(T) = -T\omega(T)$ .

In the following, we will usually suppress the index  $N$  on various quantities, unless necessary.

### C. Conditions for Equilibrium and Negative Entropy

We assume the existence of an equilibrium crystal, which has its energy  $E = E_0$  at  $T = 0$ . It also has the lowest free energy at low temperatures. Since  $E_0$  is an allowed energy, we must surely have  $W(E_0) \neq 0$ . Assuming  $TS(T) \rightarrow 0$  as  $T \rightarrow 0$ , which is always true according to the Nernst's postulate, we recognize that  $E_0$  represents not only the Helmholtz free energy but also the energy of the perfect CR at  $T = 0$ . Since  $W(E)$  is non-negative,  $Z$  is a sum of positive terms. As a consequence, the following two principles of equilibrium are always satisfied.

## 1. Principles of Equilibrium

- *Maximization Principle* The PF  $Z$  must be *maximized* in the thermodynamic limit. The maximum value of  $Z(T)$  corresponds to picking out the maximum term  $e^{S-\beta E}$  in (1). This maximum term corresponds to  $E = \bar{E}$ .
- *Stability Principle* The heat capacity, which is given by the fluctuations in the energy is non-negative.

It should be stressed that the non-negativity of the heat capacity and the maximization principle only require the *positivity* of  $W(E)$  ( $\geq 0$ );  $W(E) \geq 1$  is not required. Thus, both principles remain valid even if the entropy becomes negative [13]. The above principles of equilibrium and reality are two *independent* aspects. This observation is going to be useful when we discuss the metastable states below.

## 2. Principle of Reality

Conventional statistical mechanics for a system in the thermodynamic limit describes equilibrium states in Nature, for which the above two principles of equilibrium, along with the *principle of reality* ( $W(E) \geq 1, S(E) \geq 0$ ) must be satisfied [14]. All these conditions may not be met by metastable states. (Metastability does not occur in finite systems.) What we will see that it is the reality condition that can be violated by metastable states.

## D. Order Parameter

The presence of a melting transition at  $T_M$  (the inverse of the slope of  $HH'$  in Fig. 1) means that the *disordered* equilibrium liquid (EL) phase above  $T_M$  and the ordered CR below  $T_M$  correspond to different values of the order parameter  $\rho$ , which is traditionally defined in such a way that  $\rho = 0$  represents the disordered phase and  $\rho \neq 0$  the ordered phase CR. (Our example below will show explicitly how the microstates can be divided into the two disjoint classes.) We denote the free energy per particle above  $T_M$  by  $\omega_{\text{dis}}(T)$  [ $f_{\text{dis}}(T) = -T\omega_{\text{dis}}(T)$ ], and below  $T_M$  by  $\omega_{\text{ord}}(T)$  [ $f_{\text{ord}}(T) = -T\omega_{\text{ord}}(T)$ ], from which we can calculate the entropies, and energies per particle

$$s_\alpha(T) \equiv -(\partial f_\alpha / \partial T), \quad e_\alpha(T) \equiv -(\partial \omega_\alpha / \partial \beta), \quad (3)$$

$\alpha = \text{dis, ord}$ , respectively, corresponding to the two states. From  $s_\alpha(T)$  and  $e_\alpha(T)$ , we can construct the functions  $s_\alpha(e) \equiv s_\alpha[e_\alpha(T)]$ , where  $e = E/N$  in the thermodynamic limit. The extensive entropy functions ( $s_\alpha$  multiplied by  $N$ ) are shown schematically in Fig. 1.

## III. STATIONARY METASTABLE STATES AND RESTRICTED ENSEMBLE

### A. PL Scheme

We briefly review the restricted ensemble formalism developed by Penrose and Lebowitz [1], and the required modification to suit our purpose. Let  $e_{\text{CR},M}$ , and  $e_{\text{EL},M}$  denote the energies of the coexisting phases CR and EL at the melting temperature  $T_M$ ; see points H and H' in Fig.1. It is clear that  $s_{\text{dis}}(e)$  and  $s_{\text{ord}}(e)$  constructed above certainly exist for  $e \geq e_{\text{EL},M}$ , and  $e \leq e_{\text{CR},M}$ , respectively. Over this range, we do not need to introduce the restricted ensembles. To obtain  $s_\alpha(e)$  beyond their respective range noted above, however, we need to introduce the restricted ensembles [1].

We begin by considering the case of finite but very large  $N$ . From  $s_\alpha(e)$ , we can determine the number of microstates  $W_{\text{dis}}(E) = \exp[Ns_{\text{dis}}(E/N)] \geq 1$  consistent with  $\rho = 0$  at high temperatures (or energies  $E \geq E_{\text{EL},M} = Ne_{\text{EL},M}$ ), and the number of microstates  $W_{\text{ord}}(E) = \exp[Ns_{\text{ord}}(E/N)] \geq 1$  consistent with  $\rho \neq 0$  at low temperatures (or energies  $E \leq E_{\text{CR},M} = Ne_{\text{CR},M}$ ). (The equalities and inequalities are defined upto thermodynamically insignificant terms.) Let us focus on  $W_{\text{dis}}(E)$  for  $E \geq E_{\text{EL},M}$ , which contains only those microstates that are disordererd and correspond to  $\rho = 0$ . These microstates may contain a small number of clusters or nuclei of stable phase (CR), but their sizes are limited by the correlation length, which remains *finite* since we are dealing with a first-order transition. Let  $\xi_{\text{dis}}$  (in the units of some average inter-particle distance) denote the maximum value of the correlation length in the disordered phase. We now follow PL, and select all distinct microstates of energies  $E < E_{\text{EL},M}$ , in which there are no nuclei of the stable phase of sizes larger than  $\xi_{\text{dis}}$ , and the number of smaller clusters is not too large, i.e. is thermodynamically insignificant to ensure that these configurations also correspond to  $\rho = 0$ ; the check of this will be discussed below. We denote the number of these microstates also by  $W_{\text{dis}}(E)$ . We can similarly extend  $W_{\text{ord}}(E)$  to  $E > E_{\text{CR},M}$ . Thus, we can construct the two entropy functions  $S_{\text{ord}}(E) \equiv \ln W_{\text{ord}}(E)$ , and  $S_{\text{dis}}(E) \equiv \ln W_{\text{dis}}(E)$  that overlap, and are shown schematically in Fig.1.

### B. Required Extension

Let  $E_0$  denote the lowest energy in the system, which represents the energy of the ordered phase at  $T = 0$ . Thus,  $W_{\text{ord}}(E) \geq 1$ . While  $W_{\text{ord}}(E)$  certainly exists for microstate energies starting from  $E = E_0$ , there is no guarantee that  $W_{\text{dis}}(E)$  also exists near  $E = E_0$ . Most probably,  $W_{\text{dis}}(E)$  does not continue all the way down to  $E = E_0$ . If it did, the energy of the disordered phase at absolute zero would be  $E_0$  (we assume that  $TS_{\text{dis}} \rightarrow 0$  as  $T \rightarrow 0$ ), the same as that of CR. This would most

certainly imply that they would coexist at  $T = 0$ , each having the same volume; recall that we are considering a fixed volume ensemble. While there is no thermodynamic argument against it, it does not seem to be the case normally. Usually, the most stable state at  $T = 0$  is that of a crystal. Moreover, it is an experimental fact [5] that all glasses have much higher energies or enthalpies compared to their crystalline forms at low temperatures. Thus, we assume that the lowest possible energy  $E_K$ , see Fig. 1, for the disordered state is larger than  $E_0$ . In other words, the microstate number  $W_{\text{dis}}(E)$  has the following property:

$$W_{\text{dis}}(E) \geq 1 \quad \text{for } E \geq E_K. \quad (4a)$$

If the slope in Fig. 1 at K is finite, then there is no singularity in  $S_{\text{dis}}(E)$  at K, and we can extend it to lower energies. We assume this extension is possible and define the extended entropy function for  $E \geq E_0$ . We denote this extended entropy function by  $S_{\text{dis}}^*(E)$ , and introduce  $W_{\text{dis}}^*(E) = \exp[S_{\text{dis}}^*(E)]$ . The function  $S_{\text{dis}}^*(E)$  is identical to  $S_{\text{dis}}(E)$  over  $E \geq E_K$ . It exists over the entire range  $E \geq E_0$ , whereas  $S_{\text{dis}}(E)$  exists only over the range  $E \geq E_K$ . We can similarly extend  $W_{\text{ord}}(E)$  to  $E = E_J$ , where  $E_J$  is either equal to  $E_{\text{Max}}$ , the maximum allowed energy in the system, or the location of the singularity in  $S_{\text{ord}}(E)$  so that the latter cannot be extended beyond it. We denote this extension similarly by  $W_{\text{ord}}^*(E)$ . In the following, we are mostly interested in the extension  $S_{\text{dis}}^*(E)$ .

### C. Restricted and Extended Restricted PF's

Using  $W_{\text{ord}}(E)$ ,  $W_{\text{dis}}(E)$ , and their extended version  $W_{\text{ord}}^*(E)$ ,  $W_{\text{dis}}^*(E)$  we introduce the following *restricted ensemble* PF's [1]:

$$Z_\alpha(T) \equiv \text{Tr} W_\alpha(E) \exp(-\beta E), \quad (5a)$$

$$Z_\alpha^*(T) \equiv \text{Tr} W_\alpha^*(E) \exp(-\beta E), \quad (5b)$$

$\alpha = \text{dis}, \text{ord}$ , and the corresponding free energies

$$\Omega_\alpha(T) \equiv \ln Z_\alpha(T), \quad \Omega_\alpha^*(T) \equiv \ln Z_\alpha^*(T). \quad (6)$$

The free energy per particle  $\Omega_\alpha(T)/N$  is expected to possess a thermodynamic limit as  $N \rightarrow \infty$ , which we have already introduced earlier as  $\omega_\alpha(T)$ . The corresponding limiting free energy per particle  $\Omega_\alpha^*(T)/N$  will be denoted by  $\omega_\alpha^*(T)$ .

- *Remark* The following remark is important to understand the relationship between the starred and unstarred PF's. Let us consider the disordered PF's. For temperatures so that the average energies  $\overline{E}_{\text{dis}}^*(T)$  and  $\overline{E}_{\text{dis}}(T)$  are greater than  $E_K$ , both partition functions are determined by the microstates of energies above  $E_K$ , where the starred and unstarred  $W'_{\text{dis}}$ s are identical. Hence, for  $T \geq T_K$ , the

two PF's  $Z_{\text{dis}}^*(T)$  and  $Z_{\text{dis}}(T)$  are the same so that their free energies are the same. They differ only below  $T_K$ ; while  $Z_{\text{dis}}^*(T)$  exists there,  $Z_{\text{dis}}(T)$  does not. Similarly, for temperatures so that  $\overline{E}_{\text{ord}}^*(T)$  and  $\overline{E}_{\text{ord}}(T)$  less than  $E_J$ ,  $Z_{\text{ord}}^*(T)$  and  $Z_{\text{ord}}(T)$  are the same. Thus,

$$\omega_{\text{dis}}(T) = \omega_{\text{dis}}^*(T), \quad T \geq T_K, \quad (7a)$$

$$\omega_{\text{ord}}(T) = \omega_{\text{ord}}^*(T), \quad T \leq T_J. \quad (7b)$$

Here,  $T_J$  is the temperature where  $\overline{E}_{\text{ord}}(T) = E_J$ . The free energies  $\omega_{\text{dis}}^*(T)$  is defined for all temperatures  $T \geq 0$ .

As long as  $W_\alpha(E) > 0$ , and  $W_\alpha^*(E) > 0$ , the restricted PF's are sum of positive terms. Therefore, the corresponding free energies satisfy the two equilibrium conditions noted above. Consequently, even the restricted and extended restricted PF's will never give rise to unstable states.

It is clear that the *global maximization* of the PF requires that

$$\begin{aligned} \omega(T) &= \omega_{\text{dis}}(T) = \omega_{\text{dis}}^*(T), & T \geq T_M, \\ \omega(T) &= \omega_{\text{ord}}(T) = \omega_{\text{ord}}^*(T), & T \leq T_M. \end{aligned}$$

The switchover from  $\omega_{\text{dis}}(T)$  to  $\omega_{\text{ord}}(T)$  at  $T_M$  makes  $\omega(T)$  singular, as expected, due to the transition.

We consider the case when there is only one phase transition, the first-order melting transition, in the system. The following point is to be noted as discussed by Penrose and Lebowitz [1]. The restricted PF's defined in (5a) and (5b) require that we add an extra energy term in the energy of the system, which takes the value 0 if the microstate belongs to the set  $\alpha$ , and  $+\infty$ , if it does not. This meets the PL criterion for "static" metastable states. The other two criteria that PL require relate to the decay of metastable states, and does not have to be imposed here anymore. Thus, the problem of two incompatible requirements discussed by Penrose and Lebowitz [1] no longer is an issue.

A prescription to describe metastability using the PF formalism can now be formulated.

### D. Metastability Prescription

We *abandon* the above global maximization principle, and use  $\omega_{\text{dis}}(T)$  to give the free energy of the metastable disordered phase (supercooled liquid) below  $T_M$  and  $\omega_{\text{ord}}(T)$  to give the metastable (superheated crystal) state free energy above  $T_M$ . Similarly,  $s_{\text{dis}}(T)$ ,  $e_{\text{dis}}(T)$  and  $s_{\text{ord}}(T)$ ,  $e_{\text{dis}}(T)$  give the entropy and energy per particle for the supercooled liquid and superheated crystal, respectively.

There are two possibilities for the extrapolation of the free energy. As said above, unstable states are not possible in the restricted ensemble. Thus, either the free

energy terminates in a spinodal at a non-zero but finite temperature, or it extrapolates to  $T = 0$  through  $\omega_{\text{dis}}^*(T)$  for the supercooled liquid ( $T \rightarrow \infty$  through  $\omega_{\text{ord}}^*(T)$  for the superheated crystal). In this work, we are only interested in the supercooled liquid.

It is easy to calculate the order parameter  $\rho$  for  $T < T_M$  for the "disordered phase" by using  $Z_{\text{dis}}^*(T)$  to check if we have properly identified the set of disordered microstates above. Since all microstates in  $W_{\text{dis}}(E)$  contain only nuclei of the stable CR phase of finite sizes, the argument of Fisher [4] about the origin of an essential singularity no longer works, which requires nuclei of all sizes, including infinitely large sizes. Thus, it is clear that  $\omega_{\text{dis}}^*(T)$  can be used to describe the sought extrapolation of the free energy below the melting temperature. The phase represented by  $\omega_{\text{dis}}^*(T)$  below  $T_M$  will still correspond to a disordered state ( $\rho = 0$ ). This is our required description of SMS in the form of SCL by the PF  $Z_{\text{dis}}(T)$  below  $T_M$ .

From the above discussion, it appears highly likely that the singularity in  $\omega(T)$  does not necessarily imply a singularity in either of its two pieces  $\omega_{\text{dis}}(T)$  and  $\omega_{\text{ord}}(T)$ . Both of them can exist on either side of  $T_M$ . From the above argument, we conclude that the extrapolation used to define  $Z_\alpha^*(T)$  is not a consequence of any approximation (mean-field or otherwise). Our example below is intended to give a concrete demonstration.

The form of the entropy functions  $S_\alpha(E)$  shown in Fig. 1 is also supported by all known observations [5, 6], exact calculations [7, 15, 16], from the arguments given above and the calculation to be presented below. We note that

$$S_{\text{ord}}^*(E) < S_{\text{dis}}(E), \quad E > E_M, \quad (8a)$$

$$S_{\text{dis}}^*(E) < S_{\text{ord}}(E), \quad E < E_M, \quad (8b)$$

where  $E_M$  is the energy at A where  $S_{\text{ord}}(E) = S_{\text{dis}}(E)$ ; see Fig. 1. The SMS corresponding to the stationary SCL is defined by the branch H'ACK and its extension to  $E_0$ , which is not shown. Similarly, superheated CR is defined by the branch HAB and its extension to higher energies. We note that, as shown, the entropy  $S_{\text{dis}}$  of the metastable branch goes to zero at  $T_K > 0$  corresponding to the finite slope at K. This behavior will be supported by the exact calculation in the next section.

#### IV. EXACT 1-D CALCULATION

The calculation presented here follow the transfer matrix eigenvalue approach of Newman and Schulman [9]. We now consider a one-dimensional axis spin model, which contains  $m$ -component spins  $\mathbf{S}_i$  located at site  $i$  of the one-dimensional lattice of  $N$  sites, with periodic boundary condition ( $\mathbf{S}_{N+1} = \mathbf{S}_1$ ). Each spin can point along or against the axes (labeled  $1 \leq k \leq m$ ) of an  $m$ -dimensional spin space and is of length  $\sqrt{m}$ :  $\mathbf{S} = (0, 0, \dots, \pm\sqrt{m}, 0, \dots, 0)$ . The spins interact via a ferromagnetic nearest-neighbor interaction energy ( $-J$ ), with

FIG. 2: The bond and the entropy densities. The bond density is a monotonic function of  $T$ , so that the stability is not violated. The entropy becomes negative at low temperatures, where metastable state must be replaced by an ideal glass.

$K \equiv J/T > 0$ . The energy of the interaction is given by

$$E = -J \sum_{i=1 \dots N} \mathbf{S}_i \cdot \mathbf{S}_{i+1}.$$

The PF is given by

$$Z_N(K, m) \equiv \left(\frac{1}{2m}\right)^N \sum \exp(-\beta E) = \left(\frac{1}{2m}\right)^N \text{Tr } \hat{T}^N, \quad (9)$$

where the first sum is over the  $(2m)^N$  spin states of the  $N$  spins and  $\hat{T} \equiv \exp(K\mathbf{S} \cdot \mathbf{S}')$  is the transfer matrix between two neighboring spins. The transfer matrix has the eigenvalues

$$\lambda_{\text{dis}} = u + 2(m-1), \lambda_{\text{ord}} = v, \lambda = u-2, \quad (10)$$

that are 1-fold,  $m$ -fold, and  $(m-1)$ -fold, respectively [18]. Here we have introduced the following

$$x \equiv \exp(Km), u \equiv x + 1/x, v \equiv x - 1/x.$$

We follow de Gennes [19, 20] and provide an alternative and very useful interpretation of the above spin model in terms of a polymer system, in which each polymer has multiple bonds and loops. The valence at each site in a polymer must be even. (The presence of a magnetic field will allow odd valencies, which we do not consider here.) The high-temperature expansion of the PF, which is given by

$$Z_N(K, m) = \sum K^B m^L, \quad (11)$$

describes such a polymer system, with  $K \geq 0$ , and  $m$  denoting the activity of a bond and the activity for a loop, respectively, and  $B$  and  $L$  denoting the number of bonds

and the number of loops, respectively [20]. The empty sites represent solvent particles. The number of polymers and the number of bonds and loops in each polymer are not fixed and vary according to thermodynamics. In addition, there is no interaction between polymers, and between polymers and solvent particles, so that the polymer system in (11) is an *athermal* solution. The temperature  $T$  of the spin system does not represent the temperature in the polymer problem, as is well known [19, 20]. We will see below that small  $x$  corresponds to high temperatures where the disordered phase is present, and large  $x$  corresponds to low temperatures where the ordered and possible SMS phases are present. Thus, decreasing  $T$  amounts to going towards the region where the ordered and metastable disordered phases are present. Let  $\omega$  denote the limiting value as  $N \rightarrow \infty$  of

$$\omega_N \equiv (1/N) \ln Z_N(K, m) + \ln(2m), \quad (12)$$

where we have added an uninteresting constant to get rid of the prefactor in (9). This is done because the number of microstates appears within the summation in the spin model PF in (9). Thus, the inclusion of the prefactor will make the microstate entropy negative. The prefactor is, however, required for the polymer mapping.

The importance of the polymer mapping is that we can take  $m \geq 0$  to be a real number, even though non-integer  $m$  makes no sense for a physical spin. Thus, for non-integer values of  $m$ , only the polymer system represents a physical system. For  $m = 1$ , the axis model reduces to the Ising model, while for  $m \rightarrow 0$ , it reduces to the a model of linear chains with no loops [19, 20]. The eigenvalue  $\lambda_{\text{dis}}$  is dominant at high temperatures for all  $m \geq 0$  and describes the disordered phase. Its eigenvector is

$$\langle \chi_{\text{dis}} | = \sum_i \langle i | / \sqrt{2m},$$

where  $\langle 2k |$  ( or  $\langle 2k+1 |$ ) denotes the single-spin state in which the spin points along the positive (or negative)  $k$ -th spin-axis. It has the correct symmetry to give zero magnetization ( $\rho = 0$ ). For  $m \geq 1$ ,  $\lambda_{\text{dis}}$  remains the dominant eigenvalue at all temperatures  $T \geq 0$ . For  $0 \leq m < 1$ , the situation changes and  $\lambda_{\text{ord}}$  becomes dominant at low temperatures  $T < T_c$ , or  $[x \geq x_c = 1/(1-m)]$  where  $T_c$  is determined by the critical value  $x_c \equiv \exp(Jm/T_c)$ ; there is a phase transition at  $T_c$ . The corresponding eigenvectors are given by the combinations

$$\langle \chi_{\text{ord}}^{(k+1)} | = [\langle 2k | - \langle 2k+1 |] / \sqrt{2},$$

( $k = 0, 2, \dots, m-1$ ) which are orthogonal to  $\langle \chi_{\text{dis}} |$ , as can be easily checked. These eigenvectors have the symmetry to ensure  $\rho \neq 0$ . The remaining eigenvalue  $\lambda$  is  $(m-1)$ -fold degenerate with eigenvectors

$$\langle \chi^{(k+1)} | = [\langle 2k | + \langle 2k+1 | - (\langle 2k+2 | - \langle 2k+3 |)] / \sqrt{4},$$

( $k = 0, 2, \dots, m-2$ .) For  $m > 0$ , this eigenvalue is never dominant. For  $m \rightarrow 0$ , it becomes degenerate with  $\lambda_{\text{dis}}$ .

Since the degeneracy plays no role in the thermodynamic limit, there is no need to consider this eigenvalue separately for  $m \geq 0$ .

We now consider the limit  $N \rightarrow \infty$ . The adimensional free energy per site, which represents the osmotic pressure [7, 21], of the high-temperature equilibrium phase is  $\omega_{\text{dis}}(T) \equiv \ln(\lambda_{\text{dis}})$ . It can be continued all the way down to  $T = 0$ , even though the equilibrium osmotic pressure has a singularity at  $x_c$ . Similarly,  $\omega_{\text{ord}}(T) \equiv \ln(\lambda_{\text{ord}})$  related to the low-temperature equilibrium phase can be continued all the way up to  $T \rightarrow \infty$ . To calculate the entropy density, we proceed as follows. The bond and loop densities are given by

$$\phi_B \equiv \partial \omega / \partial \ln K, \quad \phi_L \equiv \partial \omega / \partial \ln m, \quad (13)$$

which are needed to calculate the entropy per site of the polymer system

$$s^{(P)} = \omega - \phi_B \ln K - \phi_L \ln m;$$

the superscript is to indicate that it is the polymer system entropy, and is different from the spin system entropy  $s^{(S)} = \partial T \omega / \partial T$ . If we define  $\omega$  without the last term in (12), then  $\phi_L$  and  $s^{(P)}$  must be replaced by  $(\phi_L - 1)$  and  $(s^{(P)} - \ln 2)$ , respectively. This will not affect any of the conclusions below.

In the following, we will be only interested in the polymer entropy. The proper stability requirements for the polymer system are

$$(\partial \phi_B / \partial \ln K) \geq 0, (\partial \phi_L / \partial \ln m) \geq 0, \quad (14)$$

as can easily be seen from (9), and must be satisfied even for SMS. They replace the positivity of the heat capacity of the spin system, which no longer represents a physical spin system for  $0 \leq m < 1$ . It is easy to see from the definition of  $s_{\text{dis}}^{(P)}$  that  $(\partial s_{\text{dis}}^{(P)} / \partial T)_m$  need not be positive, even if the conditions in (14) are satisfied.

Let us compute  $\omega$  as  $K \rightarrow \infty$  ( $T \rightarrow 0$ ) for the two eigenvalues  $\lambda_{\text{dis}}$  and  $\lambda_{\text{ord}}$ . From (13), it is easy to see that  $\phi_B \rightarrow mK$  for both states as  $T \rightarrow 0$ . Thus, using  $\omega = s^{(P)} + \phi_B \ln K + \phi_L \ln m$ , we have

$$\omega_{\text{dis}}(T) / \omega_{\text{ord}}(T) \rightarrow 1 \text{ as } T \rightarrow 0. \quad (15)$$

This means that if the eigenvalue  $\lambda_{\text{dis}}$  is taken to represent the metastable phase above  $x_c$ , its osmotic pressure must become equal to that of the equilibrium phase (described by the eigenvalue  $\lambda_{\text{ord}}$ ) at absolute zero. This is in conformity with Theorem 3 in [17]. We take  $\omega_{\text{dis}}(T)$  to represent the SMS osmotic pressure below  $T_c$ . We have also checked that  $T s_{\text{dis}}^{(S)} \rightarrow 0$ , as  $T \rightarrow 0$ .

We will only discuss the disordered polymer phase below for  $0 \leq m < 1$ . It is easily checked that the above stability conditions in (14) are always satisfied for  $\lambda_{\text{dis}}$ ; see, for example, the behavior of  $\phi_B$  in Fig. 2, where we have taken  $m = 0.7$ , and  $J = 1$ . Since the high-temperature disordered phase represents a physical system, it cannot

give rise to a negative entropy  $s_{\text{dis}}^{(\text{P})}$  above  $T_c$ ; however, its metastable extension violates the reality principle as shown in Fig. 2, where its entropy  $s_{\text{dis}}^{(\text{P})}$  becomes negative below  $T_K \cong 0.266$ , which is lower than the transition temperature  $T_c$ .

We now make an important observation. As  $m$  decreases (below 1), both  $T_K$  and  $T_c$  ( $T_K < T_c$ ) move down towards zero simultaneously. As  $m \rightarrow 0$ , the equilibrium ordered phase corresponding to  $\lambda_{\text{ord}}$  disappear completely, and the disordered phase corresponding to  $\lambda_{\text{dis}}$  becomes the equilibrium phase. There is no transition to any other state. Thus, there is no metastability anymore. Consequently, there is *no* ideal glass transition since there is *no* other state more ordered than this state any more, as argued above. Thus, our exact calculation confirms our earlier conclusion that the existence of an ordered state is crucial for the existence of the entropy crisis. The existence of an ordered state sets the zero of the temperature scale by its minimum energy  $E_0$ . This scale then sets the temperature  $T_K$  of the lowest SMS energy  $E_K > E_0$  to be positive.

We also observe that there is no singularity in  $\lambda_{\text{dis}}$  or  $\omega_{\text{dis}}(T)$  at  $T_c$ , even though there is a phase transition there. Similarly, there is no singularity in  $\lambda_{\text{ord}}$  or  $\omega_{\text{ord}}(T)$  at  $T_c$ . Thus, the thermodynamic singularity in the equilibrium free energy does not necessarily create a singularity in  $\omega_{\text{dis}}(T)$  or  $\omega_{\text{ord}}(T)$  at  $T_c$ , as was discussed earlier. The existence of a singularity or spinodal at some other temperature is a different matter.

## V. DISCUSSION & CONCLUSIONS

### A. SMS & Exact Calculations

The transition between SMS and the ideal glass is not brought about by any thermodynamic singularity at  $T_K$ ; rather, it is *imposed* by the reality requirement. The ideal glass state does *not* explicitly emerge as a new phase in the calculation since it is a disordered phase defined by the order parameter  $\rho = 0$ . In this sense, the transition to the ideal glass is a very special kind of transition, which does not seem to belong to the class of phase transitions in which various phases emerge in the calculation.

The exact calculation, which is not mean-field calculation in principle, in the previous section demonstrates the existence of SMS. Thus, it demonstrates that our hypothesis of SMS existence is not vacuous. It also shows that the free energy can be extrapolated below the melting temperature by the use of the restricted PF, and that there is no essential singularity, a signature of a first-order transition [4]. The free energy remains stable all the way down to absolute zero. However, the mere existence of the stable extrapolated free energy all the way down to  $T = 0$  does not mean that it represents the free energy of a realizable metastable state. This becomes evident when we consider the entropy of the extrapolated free energy. This entropy drops rapidly, and goes

through zero at  $T_K$ , and becomes negative as the temperature is reduced. A genuine entropy crisis appears in the SMS below  $T_K$ . At  $T_K$ ,  $f_{\text{dis}}^*(T_K) = E_K$ , which is higher than the CR free energy  $E_0$  at  $T = 0$ . Below  $T_K$ , the extrapolated free energy cannot represent any real metastable state and must be replaced by another free energy branch, which is constant:  $f_{\text{IG}}(T) = E_K$  for  $T < T_K$ . It is shown by the dotted horizontal straight line at K in the inset. This branch represents the free energy of the ideal glass (IG), which is the phase below  $T_K$ . We need to invoke an ideal glass transition at this temperature in the model. The energy of the ideal glass is  $E_K$ . This means that the ideal glass has a higher energy than the crystal at absolute zero, in conformity with the experiments.

It is interesting to note that  $T_K \rightarrow 0$ , as  $m \rightarrow 0$ , so that the ideal glass transition disappears. This is not surprising, as  $T_c \rightarrow 0$ . Thus, there is no ordered state anymore.

### B. No Entropy Crisis in the Equilibrium State

The entropy crisis occurs only in the metastable state, and not in the equilibrium state, even though we have not shown this explicitly here. The entropy of the latter vanishes at  $E_0$  with an infinite slope, as shown in Fig. 1. Thus, the lowest energy  $E_0$  determines the lowest allowed temperature  $T = 0$  in the system, which is consistent with the Nernst-Planck postulate. However, it is possible that the equilibrium free energy becomes horizontal, so that the entropy vanishes, over a non-zero temperature range  $(0, T_C)$  where the system is frozen. Such a situation happens, for example, in the KDP model and gives rise to a singularity at  $T_C$ . This should be contrasted with the existence of the ideal glass transition in the supercooled state, where its appearance is not accompanied by any singularity in the SMS free energy. Replacing the unphysical SMS free energy below  $T_K$  by a frozen state is done by hand; it does not emerge as part of the calculation. Indeed, as our calculation has shown, the ideal glass transition disappears as  $m \rightarrow 0$ . In this limit,  $T_c \rightarrow 0$ . Thus, the "ordered" state corresponding to  $\lambda_{\text{ord}}$  disappears, and the disordered phase remains the equilibrium state all the way down to  $T = 0$ . Thus, it is safe to conclude that equilibrium state in any system will *never* show an entropy crisis (at a positive temperature). If any exact calculation for the free energy or the entropy predicts an entropy crisis at a positive temperature, this will necessarily imply that there must exist another state, the equilibrium state, for which no entropy crisis should exist.

This observation has been crucial in a recent investigation of a dimer model [22] in which the disordered phase underwent a first-order transition to an equilibrium ordered phase. The ordered phase then gave rise to an entropy crisis at a lower temperature, which forced us to look for another equilibrium state, which was eventually discovered above the temperature where the entropy cri-

sis was found, so that the crisis occurred in a metastable state (this time emerging from an intermediate ordered state). Similar situation occurred in more complex systems containing particles of different shapes and sizes [23].

In summary, we have shown that stationary metastable

states can appear in exact calculations also. They do not only occur in mean-field calculations.

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  - [13] The stability criteria such as a non-negative heat capacity that immediately follow from the PF formulation are independent of the non-negative entropy requirement. Thus, it is possible for the SMS to have a negative en-
  - tropy over some temperature range. This will only means that such states are not observable in Nature.
  - [14] It is well known that in classical statistical mechanics, the entropy in continuum space can become negative. This is true of the ideal gas at low temperatures. From the exact solution of the classical Tonks gas of rods in one dimension, one also finds that the entropy becomes negative at high coverage. Thus, either quantum mechanics is needed or a lattice structure is needed to replace the continuum space to make entropy positive. We assume here that this has been done and that the entropy for realizable microstates cannot be negative.
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